Selective Hydrogenation of 1,3-Butadiene over LaCoO$_3$ Perovskite

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LaCoO$_3$ becomes active for hydrogenation of 1,3-butadiene upon reduction in hydrogen at temperatures between 140 and 400°C. A pulse system was used to explore the best reduction conditions to achieve high selectivity to *n*-butenes. Isomerization of these olefines does not proceed in a nitrogen atmosphere while hydroisomerization is catalyzed at similar rates to those found for hydrogenation. A gas-recirculating batch system was used for both kinetic measurements and tracer experiments. The reaction orders is 1 for hydrogen and −1 for 1,3-butadiene. The D$_2$ + 1,3 butadiene reaction product analysis shows that the diolefin is not exchanged while the *n*-butenes are extensively deuterated, its distribution exhibiting a flat maximum centered at the dideuterio species. 1-Butene is produced through 1,2-addition, according to the NMR studies. The 2-butene NMR spectra show that both vinylic and methyl hydrogens are exchanged with deuterium making it difficult to ascertain the hydrogen addition mechanism. The data accumulated on this system are consistent with metallic centers (Co^0) being the loci of hydrogenation activity. A reaction scheme is proposed which takes into account most of the experimental results.

INTRODUCTION

In the last decade several catalytic applications of mixed oxides with a perovskite structure have been explored (*1, 2*). Recently, Yasumori *et al.* (*3–5*) and Lombardo *et al.* (*6–9*) have shown the ability of a few of these compounds to catalyze both the hydrogenation and hydrogenolysis of light hydrocarbons. Among these oxides LaCoO$_3$ have been more thoroughly studied. Crespin and Hall (*10*) have shown that the lanthanum cobaltate could be reduced in hydrogen up to the point where a fine dispersion of Co^0 in La$_2$O$_3$ was obtained. Moreover, this solid could be carefully reoxidized and the original structure rebuilt with almost no loss in cristallinity. Lombardo *et al.* (*8, 9*) have reported that the cobaltate upon reduction becomes active for hydrogenation and hydrogenolysis of both ethylene and cyclopropane. The maximum activity is reached at a reduction level

which corresponds to the molecular weight formula LaCoO$_{2.25}$. These findings have led us to think that LaCoO$_3$ could become a suitable selective hydrogenation catalyst following an adequate reduction treatment.

The hydrogenation of 1,3-butadiene is a well-known test reaction which could provide a wealth of information about the activity, selectivity, and isomerization ability of a catalyst. In this work the effect of both reduction conditions and operating variables upon the catalytic properties of La CoO$_3$ were carefully studied. Deuterium tracer experiments were also performed in trying to elucidate the reaction mechanism.

EXPERIMENTAL

Catalyst preparation and pretreatment. LaCoO$_3$, having a surface area of 13 m^2/g, was prepared by the precipitation technique from an equimolar solution of La(NO$_3$)$_3$ and Co(NO$_3$)$_2$ (*10*). Before each experiment the oxide sample was given a standard *in situ* pretreatment which consisted of four 1-h steps: (i) oxidation in air

at 400°C, (ii) evacuation at the same temperature, (iii) reduction in hydrogen at a given temperature between 140 and 400°C, (iv) evacuation at 400°C. In a few of the tracer experiments the catalyst was further preexchanged with deuterium at the corresponding reduction temperature.

Gases. Hydrogen obtained from commercial sources was passed over copper wire thermostated at 300°C, anhydrous $CaCl_2$, and $MgClO_4$, and given a final cleanup with activated charcoal cooled at −195°C. Deuterium was purified through a Pd thimble. Air was dried before contacting the catalyst. 1,3-Butadiene, research grade, was further purified by fractional distillation.

Reaction procedures. Both pulse and gas-recirculating systems were used. Purified hydrogen flowed through the pulse reactor at atmospheric pressure. A constant-volume dosimeter (3.59 cm³) allowed the injection of measured amounts of the hydrocarbon reactant, either 1,3-butadiene or *n*-butene isomer. Both the kinetic measurements and tracer experiments were performed in the batch system whose total volume was 430 cm³. This system had a mixing bulb, a reactor bypass to provide good mixing of the reactants before contacting the catalyst and a 2-cm³ sampling loop for the on-line GC analysis. The reaction temperature was in most cases lower and in a few runs equal to that used during reduction.

Mass spectrometer and NMR measurements. The reaction products were separated by GC and collected in a trap cooled at −196°C. The mass spectra were taken at 12.5 eV to reduce the cracked species to below 1% of the parent peak. The NMR spectra were obtained using a 80-MHz F.T. Bruker spectrometer with double irradiation capability. Both deuterated chloroform and dimethyl sulfoxide were used as solvents.

RESULTS

Hydrogenation of 1,3-Butadiene in the Pulse System

This type of experiments was run with the main goal in mind of exploring the best reduction conditions to achieve the highest selectivity to *n*-butenes. These experiments provided information about clean surface behavior of the catalyst at high hydrogen-to-butadiene ratio, otherwise the most unfavorable conditions to achieve good selectivity.

The results obtained at different reduction and reaction temperatures are shown in Table 1.

The conversion was defined as

$$x = \frac{(\Sigma n_{C_4H_8}) + n_{C_4H_{10}}}{(\Sigma n_{C_4H_8}) + n_{C_4H_{10}} + n_{C_4H_6}}.$$

The *n*-butene selectivity was calculated as

$$S = \frac{(\Sigma n_{C_4H_8})}{(\Sigma n_{C_4H_8}) + C_4H_{10}}.$$

Variations in either the slug size (0.17 to 0.86 cm³ STP) or the space velocity (0.4 to 11 cm³/g sec) did not modify the conversion and the product distribution. They did not change either after several slugs of reac-

TABLE 1

1,3-Butadiene Hydrogenation in a Pulse Reactor[a]

Reduction temperature (°C)	Reaction temperature (°C)	Conversion x	Selectivity S
147	143	0.30	1.00
160	143	0.44	0.93
175	175	0.97	0.65
186	130	0.12	1.00
	186	1.00	0.86
190	126	0.26	1.00
	143	0.50	0.94
	190	1.00	0.45
215	143	0.87	0.54
232	143	1.00	0.32
258	143	1.00	0.17
267	77	1.00	0
	132	1.00	0
400	0	1.00	0
	180	1.00	0

[a] Amount of $LaCoO_3$: 500 mg; H_2 flow rate: 50 cm³/min; 1,3-butadiene pulse: 0.3 cm³ STP.

tants were sent through the reactor, as long as the reaction temperature was kept below that used in the reduction.

Table 1 shows that for any given reduction condition there is an inverse relationship between activity and selectivity as a function of reduction temperature. When both the reduction and reaction temperature were the same the catalytic activity increased and the selectivity decreased with time on stream.

Figure 1 shows the catalytic behavior of LaCoO₃ reduced at various extents at a constant reaction temperature of 143°C. Higher conversion and lower selectivities were obtained as the reduction temperature increased. When this reached 230°C small amounts of hydrogenolysis products were detected. Around 260°C the catalyst became extremely active and the almost exclusive product detected was C_4H_{10}. It is also seen in Fig. 1 that the 1-butene/2-butene ratio remained constant at high selectivities and started to fall around the same point the selectivity began to move downward.

The pulse experiments have shown that the catalyst could operate at optimum selectivity at reduction temperatures between 140 and 190°C as long as the reaction temperature was accordingly adjusted. At these low temperatures the extent of reduction is below 0.2 electrons/molecule (La-

$CoO_{2.9}$) and cannot be calculated by measuring the hydrogen uptake in the gas-recirculating system, due to the small amount of hydrogen consumed. In fact the extent of reduction could be determined in a volumetric system when the temperature exceeded 250°C (11).

Since the optimum pretreatment temperature range was relatively low it was further checked if the catalyst could be activated by evacuation at 450°C. No activity developed at reaction temperatures below 140°C in the first few pulses.

n-Butene Isomerization (Pulse System)

The isomerization of both 1-butene and cis-2-butene were carried out in nitrogen flow under the same conditions which yielded good selectivity for hydrogenation. No detectable conversion was observed in these experiments. However, when nitrogen was substituted with hydrogen the isomerization proceeded readily. A sample experiment is shown in Table 2 in which the slug of 1,3-butadiene was injected between two pulses of n-butenes. It should be noted that the trans/cis ratio was the same when the reactants was either 1,3-butadiene or 1-butene.

1,3-Butadiene Hydrogenation in Batch System

In these experiments the H₂/hydrocarbon ratio could be controlled at will. At low ratios (1 to 4) the reduction temperature could be increased up to 250°C without loss in selectivity. Figure 2 shows the results obtained with a $H_2:HC = 2:1$ mixture at 140°C reaction temperature. The plot is characteristic of a series reaction system, the main difference being that the second reaction (production of n-butane) was negligible as long as 1,3-butadiene was present in the reacting atmosphere. The n-butene product distribution followed the same trend as in the pulse experiments, i.e., 1-butene > trans-2-butene > cis-2-butene at high selectivities, while 1-butene rapidly
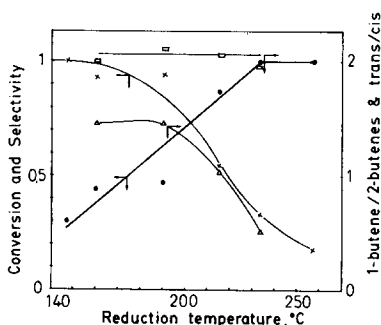

FIG. 1. The effect of reduction temperature of La CoO₃ upon the product distribution of 1,3-butadiene hydrogenation. Pulse reactor, 0.5 g of LaCoO₃, H₂ flow rate 50 cm³/min. (●) Conversion, (×) selectivity, (△) 1-butene/2-butenes, (□) trans/cis.

TABLE 2

Hydroisomerization of $n_{C_4H_8}$ on $LaCoO_3{}^a$

Pulse No. (reactant)	Reduction temperature (°C)	Reaction temperature (°C)	x	S	% Isom.	$\dfrac{trans}{cis}$
1 (1-C_4H_8)	185	177	0.23	—	16.5	1.8
2 ($1,3$-C_4H_6)	185	177	0.83	0.86	—	1.75
3 (cis-2-C_4H_8)	185	177	0.49	—	36.0	—

^{a} Experimental conditions, see Table 1.

decreased by the time the diolefin had almost disappeared.

At higher H_2/HC ratios the rate of reaction increased and the maximum concentration of 1-butene shifted to lower reaction times while the n-butane formation started earlier.

To ascertain the extent of deactivation of the catalyst, two successive runs were performed at a reaction temperature of 143°C using H_2 : HC = 1 : 1 mixtures. The catalyst was reduced at 250°C. After the first run the reactor was evacuated at 140°C and a second load of reactants was admitted. In both cases a plateau was reached after 100 min of reaction time at a conversion level around 60–70%. The second run was slightly slower than the first but the product distribution was exactly the same. These results show that little deactivation occurred between runs and it could not explain the plateau of the conversion plots.
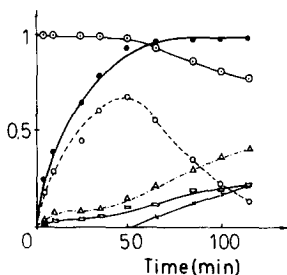

FIG. 2. 1,3-Butadiene hydrogenation over $LaCoO_3$ reduced at 250°C. Batch reactor, reaction temperature 140°C, P_T = 150 Torr, H_2/HC = 2. (●) Conversion, (⊙) selectivity. Mass fraction of (○) 1-butene, (□) cis-2-butene, (×) butane, (△) $trans$-2-butene.

Therefore it is likely that this effect was produced by the strong chemisorption of 1,3-butadiene which blocked the hydrogen adsorption when its partial pressure decreased below a critical value.

The concentration reaction order was determined by extrapolation at zero conversion through systematic variation of the H_2/HC ratio while keeping constant either the hydrogen or the 1,3-butadiene partial pressure. The global kinetic expression obtained was

$$r = k_g \frac{P^0_{H_2}}{P^0_B}$$

The strong chemisorption of the diolefin is again reflected in the rate equation.

Tracer Experiments

Figure 3a shows the deuterated product distribution obtained at 40% conversion and unit selectivity after an experiment with a D_2 : HC = 2 : 1 mixture. The full line bars correspond to the experimental results and the broken line ones to the mole fractions calculated assuming a binomial distribution. The unreacted 1,3-butadiene showed no deuterated compounds. The data shown in Fig. 3b correspond to a duplicate experiment in which, after hydrogen reduction, the catalyst was exchanged with deuterium for 1 h at 250°C. It should be noted that in both tracer experiments the 1-butene product showed a higher deuteration than the 2-butene isomers.

Figure 4a shows a sample NMR spectrum of the deuterated 1-butene product.
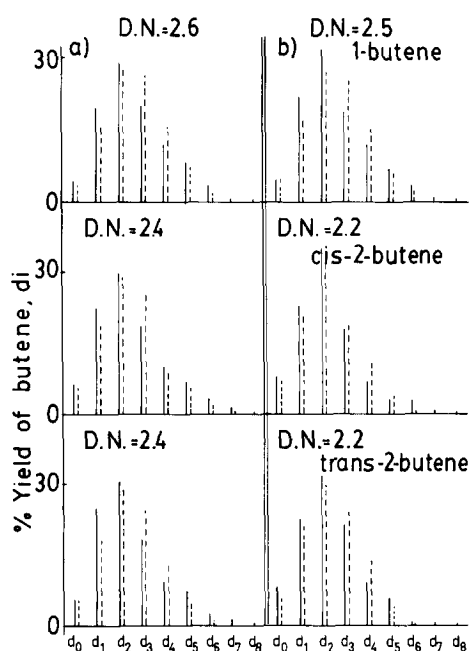
FIG. 3. Isotopic distribution of *n*-butenes produced by the reaction of a $D_2 : 1,3\text{-}C_4H_6 = 2:1$ mixture over $LaCoO_3$ reduced at 250°C in H_2. Batch reactor, reaction temperature 140°C, $P_T = 225$ Torr. (a) Final conversion 40%. (b) Before reaction the catalyst was exchanged with D_2 for 30 min at 250°C. Final conversion 30%.

The reduction of the intensity ratio and the change in multiplicity of both the $-CH_3$ and $-CH_2-$ signals clearly indicate that the deuterium has been almost exclusively incorporated into these groups. This conclusion has been further confirmed through double resonance tuned to the $-CH_2-$, $-CH_3$, and $=CH_2$ groups. The irradiation of the $-CH_2-$ group (Fig. 4b) gave rise to a wider $-CH_3$ signal due to the coupling with the deuterium atoms present in the methylene group. When the methyl hydrogens were irradiated the same results were obtained for the $-CH_2-$ group (Fig. 4c).

The spectra of the vinylic hydrogens show a slight modification in their multiplicity (Fig. 4a) due to the deuterium atoms present in the $-CH_2-$ group. When this was irradiated (Fig. 4b) the conclusion was reached that no detectable amount of deuterium has been exchanged into the vinylic positions. Figure 4d confirms the previous analysis.

The NMR results lead to the conclusion that the 1-butene product has been formed by 1,2-addition, while at the same time the hydrogen atoms located in these positions were rapidly exchanged with the pool of hy-
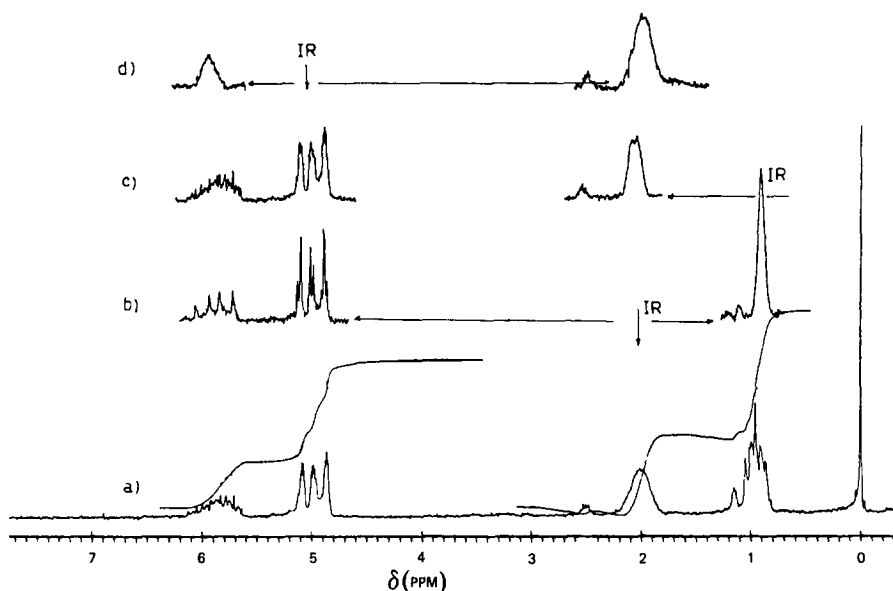

FIG. 4. NMR spectra of 1-butene produced in the deuteration of 1,3-butadiene. For reaction conditions see Fig. 3.

drogen and deuterium that populated the surface once the reaction had started. This fast equilibration was responsible for the broad distribution (almost binomial) of deuterated products which include d_0 and d_1 compounds. Consistent with this model is the very low proportion of d_6-d_8 species (Fig. 4) since five deuterium atoms is the maximum number that can be introduced into the saturated carbons of the 1-butene.

The NMR spectra of both cis and trans-2-butene look very much alike (Fig. 5). Both the intensities and multiplicities of the signals indicate that deuterium was present in the vinylic as well as in the terminal positions, the former showing a higher degree of exchange than the latter. Due to the existence of only two different group in the 2-butene molecule and the presence of several polideuterated species it is difficult to ascertain whether a 1,4- or 1,2-addition plus isomerization is the mechanism through which these isomers are formed.
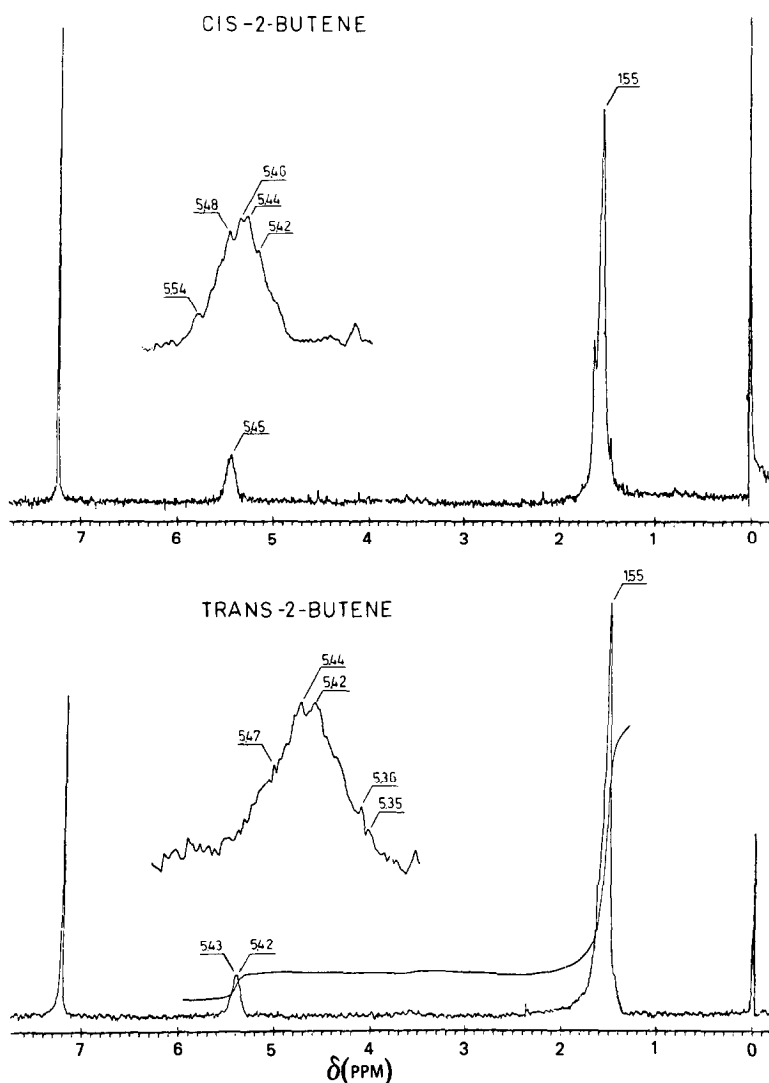

FIG. 5. NMR spectra of cis and trans-2-butene produced in the deuteration of 1,3-butadiene. For reaction conditions see Fig. 3.

DISCUSSION

The Nature of Active Sites

Most experimental evidences indicate that metallic centers (Co^0) produced during the activation step are the loci of hydrogenation activity. However, the rest of the surface also seems to play a role in the development of the catalytic properties.

At the low reduction temperatures needed to activate the $LaCoO_3$ (Table 1) the percentage of Co^0 on the surface was estimated to be below 5% (11). Therefore, it is conceivable to think that the active sites could be oxidic in nature. One point against this possibility is the fact that this solid did not become active after evacuation at 450°C as is usually the case for oxide catalysts, e.g., Co_3O_4 (12). Another argument arises from the analysis of the product distribution reported in Table 3 which shows that $LaCoO_3$ behaves more like supported cobalt (13) than either cobalt or lanthanum oxide (14, 15). Besides, it has been previously shown using several test reactions, adsorption studies, and XPS (8, 9, 11) that the active sites are essentially Co^0 clusters that develop upon reduction. The maximum in catalytic activity for the reactions of hydrogen with either ethylene or cyclopropane appeared after reduction at 350°C. At this point the concentration of Co^0 on the surface reached its highest value (11).

The behavior of reduced $LaCoO_3$ in 1,3-butadiene hydrogenation is consistent with the previous studies, e.g., at low reduction temperatures (<250°C) a small concentration of Co^0 on the surface favors higher selectivity which then falls down as the extent of reduction increases. The fact that industrial Pd/Al_2O_3 catalysts which show high selectivity contain small amounts of metal (<0.1%) at low dispersion, falls in line with these views.

It is not possible at this point, however, to dismiss the role of the rest of the surface in the catalytic process. One could speculate that the hydrocarbon molecule may be strongly adsorbed at coordinatively unsaturated sites while hydrogen is bonded to neighboring metallic clusters. An experimental fact that could support this model is the much stronger chemisorption of 1,3-butadiene on $LaCoO_3$ than on metals (13, 16–18) which was also reflected in the absence of deuterated butadienes, despite the fact that the butene products showed an almost statistical distribution of deuterated species. On the other hand, these latter results give additional support to the role played by metallic centers, for the deuterium distributions shown in Fig. 3 are similar to those reported by Phillipson et al. (13) when 1,3-butadiene was reacted with D_2 over Co^0. Besides, it is well known that most oxide catalysts give close to 100% d_2,

TABLE 3

Hydrogenation of 1,3-Butadiene over Various Catalysts

Catalyst	Reduction temperature (°C)	Reaction temperature (°C)	$n_{C_4H_8}$ distrib.	1-Butene / 2-Butenes	trans / cis	S
Co_3O_4 (14)	—	r.t.	$t \simeq c > 1$	0.25	1	1
La_2O_3 (15)	—	0	$t > c > 1$	Very low	>5	1
$Co/Al_2O_3{}^a$ (13)	329	106	$1 > t > c$	1.1	2	1
$LaCoO_3{}^b$	160	143	$1 > t > c$	1.73	2	0.93
$LaCoO_3{}^c$	250	143	$1 > t > c$	2.2	1.7	1

[a] Reduced at temperatures >400°C the product distribution was modified.
[b] Pulse reactor.
[c] Batch reactor.

butenes under similar conditions (*15, 19–23*). Previous studies of the ethylene deuterogenation over oxides have also shown that the main product was d_2, ethane (*24–26*).

Reaction Mechanism

The most important features of the hydrogenation reaction are summarized:

—The presence of 1,3-butadiene in the batch system completely inhibits both the isomerization of butenes and its hydrogenation to butane (Fig. 2).

—The negative order of 1,3-butadiene, the absence of deuterated diolefin in the gas phase and the previous inhibitory effect demonstrate that this reactant is very strongly adsorbed.

—1-Butene is formed through a 1,2 hydrogen-addition mechanism according to the NMR spectra (Fig. 4).

—The 2-butenes do not seem to be produced through isomerization of 1-butene at high selectivity. Supporting this view is the slightly higher average number of deuterium found in 1-butene than in both 2-butenes (Fig. 3).

—*n*-Butene isomerization does not proceed in the absence of hydrogen.

—The *trans/cis* ratio in 1-butene hydro-isomerization is very close to that found in 1,3-butadiene hydrogenation (Table 2).

In view of these experimental facts a reaction mechanism can be advanced which is shown in Fig. 6. To simplify the picture the hydrocarbon–deuterium exchange was not included in the model.

The existence and interconversion of the various forms of adsorbed 1,3-butadiene have been discussed by others (*27*). Basically this mechanism implies the formation of 1-butene via 1,2-addition while along this line *cis*- and *trans*-2-butene should be produced through isomerization of the former. If this were the case the average number of deuterium atoms in the 2-butenes should be higher than in the 1-olefin. The MS data (Fig. 3) show this not to be the case. Therefore in the first stage of the reaction the
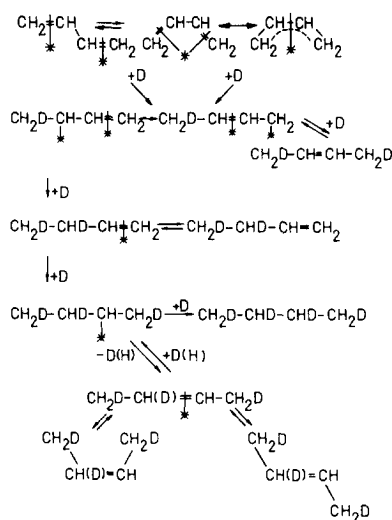

FIG. 6. Reaction mechanism of 1,3-C_4H_6 hydrogenation and *n*-butene isomerization over reduced La CoO_3.

most probable mechanism for 2-butene formation is 1–4 addition (see right side of Fig. 6). Only when the 1,3-butadiene pressure reaches a very low value the 2-butenes are produced through 1-butene isomerization (note the change in slope of 2-butene concentration at this point in Fig. 2). The strong 1,3-butadiene adsorption supports this model. Once the 1-butene is formed it is rapidly displaced from the surface by the diolefin and cannot be either isomerized or hydrogenated. This competition is suppressed at very low partial pressure of the diolefin. The 1-butene can be then readsorbed and converted to 2-butenes and butane. This is also consistent with the effect observed when a $H_2 : HC = 1 : 1$ mixture was used, e.g., at low partial hydrogen pressure the reaction stopped.

It should be noticed that the two resonance hybrids in the second line of Fig. 6 could be as well represented by a π-bonded allyl intermediate in the way pictured by Meyer and Burwell (*28*). In fact, when they hydrogenated 1,3-butadiene over Pd/Al_2O_3 they did find almost identical distribution patterns of both 1-butene and *trans*-2-butene products, much the same as in our case (Fig. 3).

The predominance of 1,2 over 1,4 hydrogen addition could be understood in terms of the low hydrogen concentration on the surface. This could mean a higher probability of finding two hydrogen atoms near a single double bond than in such a favorable position as to enter in both extremes of the hydrocarbon molecule.

This work has shown that through an adequate control of the activation (reduction) pretreatment of $LaCoO_3$ a highly selective hydrogenation catalyst can be obtained. The presence of low concentration of Co^0 on the surface plays a fundamental role in this catalyst, in line with previous findings (8, 9, 11). The overall reaction mechanism has been fairly well understood, except for the formation of small amounts of 2-butenes, possibly through parallel 1,4-addition, under conditions of high selectivity. This side of the problem requires further research.

ACKNOWLEDGMENTS

REFERENCES

1. Voorhoeve, R. J. H., in "Advanced Materials in Catalysis" (J. J. Burton and R. L. Garten, Eds.), Chap. 5. Academic Press, New York, 1977.
2. Voorhoeve, R. J. H., Johnson, D. W., Jr., Remeika, J. P., and Gallagher, P. K., Science 195, 827 (1977).
3. Ichimura, K., Inoue, Y., Kojima, I., Miyazaki, E., and Yasumori, I., "Proceedings, 7th International Congress on Catalysis, 1980," Part B, p. 1281 (1981).
4. Ichimura, K., Inoue, Y., and Yasumori, I., Bull. Chem. Soc. Jpn. 53, 3044 (1980).
5. Ichimura, K., Inoue, Y., and Yasumori, I., Bull. Chem. Soc. Jpn. 54, 1787 (1981).
6. Petunchi, J. O., Nicastro, J. L., and Lombardo, E. A., J. Chem. Soc. Chem. Commun. 467 (1980).
7. Petunchi, J. O., Ulla, M. A., Nicastro, J. L., and Lombardo, E. A., "Proceedings, 7th Iberoamerican Symposium on Catalysis, 1980," p. 108.
8. Petunchi, J. O., Ulla, M. A., Marcos, J. A., and Lombardo, E. A., J. Catal. 70, 356 (1981).
9. Ulla, M. A., Miró, E., and Lombardo, E. A., "Proceedings, 8th Iberoamerican Symposium on Catalysis, 1982," p. 475.
10. Crespin, M., and Hall, W. K., J. Catal. 69, 359 (1981).
11. Lombardo, E. A., Tanaka, K., and Toyoshima, I., J. Catal. 80, 340 (1983).
12. Fukushima, T., and Ozaki, A., J. Catal. 32, 376 (1974).
13. Phillipson, J. J., Wells, P. B., and Wilson, G. R., J. Chem. Soc. A 1351 (1969).
14. Tanaka, K., and Okuhara, T., J. Catal. 65, 1 (1980).
15. Imizu, I., Sato, K., and Hattori, H., J. Catal. 76, 65 (1982).
16. Bond, G., Webb, G., Wells, P., and Winterbottom, J., J. Chem. Soc. 3218 (1965).
17. Wells, P. B., and Bates, A. J., J. Chem. Soc. A 3064 (1968).
18. Bates, A. J., Leszczynsky, Z. K., Phillipson, J. J., Wells, P. B., and Wilson, G. R., J. Chem. Soc. A 2435 (1970).
19. Naito, S., Sakurai, Y., Shimizu, H., Ohnishi, T., and Tamaru, K., Trans. Faraday Soc. 67, 1529 (1971).
20. Hattori, H., Tanaka, Y., and Tanabe, K., J. Amer. Chem. Soc. 98, 4652 (1976).
21. Imizu, Y., Tanabe, K., and Hattori, H., J. Catal. 56, 303 (1979).
22. Yamaguchi, T., Hightower, J. W., J. Amer. Chem. Soc. 99, 4201 (1977).
23. Okuhara, T., Kondo, T., and Tanaka, K., J. Phys. Chem. 81, 808 (1977).
24. Burwell, R. L., Littlewood, A. B., Cardew, M., Pass, G., and Stoddart, C. T. H., J. Amer. Chem. Soc. 82, 6272 (1960).
25. Conner, W. C., Innes, R. A., and Kokes, R. J., J. Amer. Chem. Soc. 90, 6858 (1968).
26. Tanaka, K., Nihira, H., and Ozaki, A., J. Phys. Chem. 74, 4510 (1970).
27. Bond, G., and Wells, P. B., in "Advances in Catalysis" (D. D. Eley, H. Pines, and P. B. Weisz, Eds.), Vol. 15, p. 196. Academic Press, New York, 1964.
28. Meyer, E. F., and Burwell, R. L., J. Amer. Chem. Soc. 85, 2886 (1963).